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(54) STABILIZER FOR POLYVINYL CHLORIDE RESIN
AND POLYVINYL CHLORIDE RESIN
COMPOSITION

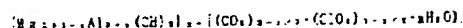
one carbon atom.

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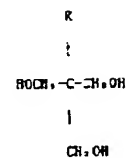
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PROBLEM TO BE SOLVED: To obtain a composition showing good thermostability and initial discoloration by incorporating hydrotalcite compounds treated with perchloric acid, a stabilizer containing one or more of trimethylol compounds and/or their condensation products and no heavy metal into a polyvinyl chloride resin.

SOLUTION: A resin composition comprises 100 pts.wt. of polyvinyl chloride resin; 0.01-5 pts.wt. of hydrotalcite compounds treated with perchloric acid; a predetermined amount of a stabilizer containing 0.01-5 pts.wt. of one or more of trimethylol compounds and/or their condensation products and no heavy metals such as Zn, Cd, Ba, Sn and Pb. The hydrotalcite compounds treated with perchloric acid are lamellar compounds having a composition represented by formula I. The trimethylol compounds are compounds represented by formula II and/or their condensation products including trimethylol propane. In the formulas, X is a positive number not more than 0.33; m is a positive number; and R is an organic residue such as an alkyl group having at least



I



II

JAPANESE

[JP,2000-026687,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE
INVENTION TECHNICAL PROBLEM MEANS EXAMPLE

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1] The stabilizing agent for polyvinyl chloride resins characterized by not including heavy metal, such as Zn, Cd, Ba, Sn, and Pb, on the parenchyma, including at least one or more sorts chosen out of the condensate of perchloric acid processing hydrotalcite compounds, and ***** roll compounds and/or those ***** roll compounds.

[Claim 2] A polyvinyl chloride resin and the polyvinyl chloride resin system constituent characterized by containing the stabilizing agent for polyvinyl chloride resins according to claim 1.

[Claim 3] At least one or more sorts chosen out of the condensate of the perchloric acid processing hydrotalcite compounds in the aforementioned stabilizing agent for polyvinyl chloride resins, ***** roll compounds, and/or those ***** roll compounds of blending ratio of coals are 0.01-5:0.01-5 in a weight ratio. The blending ratio of coal of a-izing agent receives the polyvinyl chloride resin 100 weight section. and the aforementioned object for a polyvinyl chloride resin -- a law -- It is 0.02 - 10 weight section in a total quantity conversion with at least one or more sorts chosen out of the condensate of perchloric acid processing hydrotalcite compounds, ***** roll compounds, and/or those ***** roll compounds. The polyvinyl chloride resin system constituent characterized by not including heavy metal, such as Zn, Cd, Ba, Sn, and Pb, on the parenchyma.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention does not relate to the polyvinyl chloride resin system constituent with a good stability to a thermal stability (especially initial tincture nature), and relates to the stabilizing agent for polyvinyl chloride resins and polyvinyl chloride resin system constituent which do not contain heavy metal, such as Zn, Cd, Ba, and Sn, during combination composition in detail.

[0002]

[Description of the Prior Art] To heat and light, a polyvinyl chloride resin is an unstable resin and tends to cause a tincture degradation by the pyrolysis which mainly originated in the dehydrochlorination especially at the time of a fabricating operation. Addition of a stabilizer is made into **s for elimination of the degradation factor by the heat at the time of this fabricating operation etc., or reduction-izing.

[0003] Conventionally, stabilizers, such as compound metallic-soap systems, such as a lead system, and Ba, Zn, calcium, and an organic tin system, are used, and further, an epoxy compound, the organic phosphorous-acid ester compound, beta-diketone compound, the polyhydric-alcohol compound, the nitrogen-containing compound, etc. used together, and have been used.

[0004] It is increasing, when used for the intended use which the intended use of PVC is expanded and dislikes contamination by heavy metal, such as a semiconductor industrial facility relation and a food-stuff-industry facility relation, to a degree very much in recent years.

[0005] For example, in semiconductor manufacturing facility relations (a cleaning equipment, etching system, etc.), the various processings in process must be carried out, it will be in process, these metals will be eluted, and the polyvinyl chloride resin which contains heavy metal compounds, such as Pb, Sn, and Zn, as a stabilizer will affect electronic parts etc. For this reason, not to contain heavy metal is desired in the resin constituent for semiconductor manufacturing facilities.

[0006] conventionally, the tubing material used for ultrapure-water piping for plants etc. lessens irregularity of an inside-a-hall side as much as possible, and obtains a smooth front face -- as -- manipulation speed -- dropping -- metal mold -- inner pass time -- more than twice -- it is applying and fabricating Therefore, in response to the heat history, it becomes easy to disassemble a resin. Moreover, since a productivity is also very bad, the study in a combination side is performed.

[0007] Moreover, although it is indicated conventionally that combined use of ** -ized alcohol, dihydroxy pyridines, or beta-amino crotonic-acid ester adds an amino carboxylic acid to JP,62-197439,A as non-metal combination at JP,62-273243,A, in the above-mentioned non-metal resin constituent, the heat stabilization of any cannot fully be carried out, but it is easy to color them.

[0008] Moreover, the vinyl-chloride-resin constituent which JP,7-278389,A is made to contain so that the proportion of the perchloric acid anion to a carbonic acid anion may become a 1.6-30wt time, and becomes, and is characterized by Zn salt of an organic acid, Cd salt, Pb salt, and not carrying out organic Sn compound inclusion is indicated. However, even if it bore the powder slush molding which there is much plasticizer and is blended, like a pipe and a hard variant article, since high shearing force was applied, it was easy to color and was inadequate [the above-mentioned constituent / the heat history was large, and] in non-plastic or extrusion molding with little plasticizer, practical.

[0009] Moreover, if zinc compounds, such as a zinc stearate, are not used together as illustrated by the example although the chlorination vinyl-polymer constituent with which 5-15, and the number of hydroxyl groups are characterized [a ditrimethylol propane and a carbon atomic number] by consisting of the combination with the polyol below 100 degreeC by the melting point by 2-10 is indicated by JP,57-151637,A, tincture is remarkable, and good mold goods were not obtained. Moreover, although the stabilizing agent which comes to contain zinc soap and ***** rolls in JP,9-151288,A was indicated, it was ineffective and combined use of zinc soap was [a ***** rolls independent] indispensable.

[0010] Moreover, although adding the partial ester and the halogen oxygen-acid salt of the metal salt of an organic acid and ** -ized alcohol was indicated by JP,58-127751,A, if each example was using Zn compound together and did not use Zn compound together, a good hue was not acquired but it was inadequate.

[0011]

[Problem(s) to be Solved by the Invention] It is the stabilizer combination which does not contain heavy metal, and is offering the polyvinyl chloride resin constituent in which a good thermal stability and initial tincture nature are shown.

[0012]

[Means for Solving the Problem] As a result of this invention person's etc. repeating a study zealously in view of such status, by combining the condensate of (a) perchloric acid processing hydrotalcite compound, (b) ***** roll compounds, and/or ***** roll compounds, excluding heavy metal compounds, such as Zn compound, Cd compound, Ba compound, Pb compound, and Sn compound, it found out that the polyvinyl chloride resin system constituent which is excellent in the thermal resistance with a good hue was obtained, and ** also reached this invention.

[0013]

[Embodiments of the Invention] Hereafter, this invention is explained in detail. The stabilizing agent of this invention A polyvinyl chloride resin, for example, the homopolymer of a vinyl chloride, The copolymer which makes a vinyl chloride a principal component, a chlorinated polyethylene, a polyvinylidene chloride, As opposed to the mixture (polymer blend) of chlorination polypropylene, these mixtures or the above-mentioned polymer, and other polymers etc. It is the

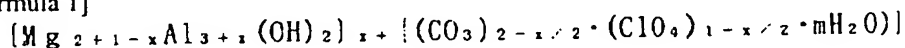
stabilizing agent which can give the thermal resistance which did not blend heavy metal compounds, such as Zn compound, Cd compound, Ba compound, Pb compound, and Sn compound, but was excellent also in **. Perchloric acid processing hydrotalcite compounds It is characterized by containing at least one or more sorts chosen out of the condensate of ***** roll compounds and/or those ***** roll compounds.

[0014] As a polyvinyl chloride resin used with the polyvinyl chloride resin system constituent of this invention, it is the mixture (polymer blend) of the homopolymer of a vinyl chloride, the copolymer which makes a vinyl chloride a principal component, a chlorinated polyethylene, a polyvinylidene chloride, chlorination polypropylene, these mixtures or the above-mentioned polymer, and other polymers etc., for example. Specifically, they are a polyvinyl chloride and vinyl acetate-vinyl chloride copolymer, an ethylene-vinyl chloride copolymer, a propylene-vinyl chloride copolymer, an ethylene-vinyl acetate-vinyl chloride copolymer, an acrylic-ester-vinyl chloride copolymer, etc. As an example of the polymer which does not contain a vinyl chloride, they are an ethylene-vinyl acetate copolymer, an ethylene-vinyl acetate-1 carbon-monoxide copolymer, an acrylic-ester polymer, a meta-acrylic ester-butadiene-styrene graft copolymer, or a special polyurethane resin.

[0015] Moreover, as perchloric acid processing hydrotalcite compounds used by this invention, the stratified compound shown, for example by ** 1 is mentioned.

[0016]

[Formula 1]



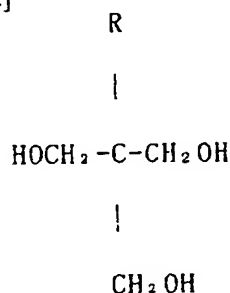
(式中 m は正の数を、x は 0.33 以下の正の数を表す)

[0017] moreover -- addition number of copies of the perchloric acid processing hydrotalcite compounds used by this invention ***** -- the polyvinyl chloride resin 100 weight section -- receiving -- 0.01 to 5 weight section -- it is preferably used in the domain of 0.03 to 3 weight section The effect over a thermal stability is scarce, and even if it uses it exceeding 5 weight section, it is deficient in the increase-in-quantity effect at less than 0.01.

[0018] Moreover, the ***** roll compounds used by this invention are shown by ** 2, and a monomer and/or its condensation product are mentioned.

[0019]

[Formula 2]



上記一般式 (2) において、R は炭素数 1 以上のアルキル基等の

有機残基を示す。

[0020] As an example of ***** roll compounds and the condensate of those, ***** roll ethane, a trimethylol propane, ***** roll butane, a ***** roll hexane, a ***** roll octane, ditrimethylol ethane, a ditrimethylol propane, a ditrimethylol hexane, a tris trimethylol propane, a poly-trimethylol propane, etc. are mentioned.

[0021] moreover -- the ***** roll compounds used by this invention, and addition number of copies of the condensate ***** -- the polyvinyl chloride resin 100 weight section -- receiving -- 0.01 to 5 weight section -- it is preferably used in the domain of 0.03 to 3 weight section The effect over a thermal stability is scarce, and even if it uses it exceeding 5 weight section, it is deficient in the increase-in-quantity effect at less than 0.01.

[0022] The polyvinyl chloride resin in this invention can be made to contain the various additives usually used in the domain which does not spoil the effect of this invention. It is not the object limited especially as an additive. For example, a plasticizer, a lubricant, processing aid, a reinforcement and a stabilization assistant (organic phosphite, an epoxy compound, and an antioxidant --) The flame retarder as functional grant agents, such as a diketone and perchloric acid salts, an antistatic agent, Although the metallic oxide as a pigment, a metal complex compound, a metal-containing pigment, etc. are mentioned further, the metal salts which do not contain the heavy metal as an ultraviolet ray absorbent, a light stabilizer, a foaming agent, and a thermostabilizer, the inorganic compound as a bulking agent, and the thing which does not contain heavy metal are desirable.

[0023] As a plasticizer which can be used with the polyvinyl chloride resin system constituent of this invention, epoxy compounds, such as dialkyl free-wheel-plate rates, dialkyl horse mackerel peats, dialkyl sebacate, polyester system plasticizers that make an adipic acid a principal component, organic phosphoric ester, chlorinated paraffin and epoxidation soybean oil, and the epoxidation linseed oil, are mentioned, for example.

[0024] As a lubricant which can be used with the polyvinyl chloride resin system constituent of this invention, the paraffine-wax, liquid paraffin, polyethylene wax, polypropylene wax, montanoic-acid wax, higher-fatty-acid, high-class fatty-alcohol, and fatty-acid flax id, fatty acid ester, etc. are mentioned, for example.

[0025] As processing aid which can be used with the polyvinyl chloride resin system constituent of this invention, that which has mainly been entitled, for example by tradenames, such as the money ace of Kanegafuchi Chemical Industry Co., Ltd. of an acrylic resin, meta-***** of Mitsubishi Rayon Co., Ltd., and Palaloid of Kureha Chemical Industry Co., Ltd., is mentioned.

[0026] As a reinforcement which can be used with the polyvinyl chloride resin system constituent of this invention, an acrylonitrile-styrene-butadiene-rubber resin, a methylmetaacrylate-styrene-butadiene-rubber resin, an acrylic resin,

butadiene resins, a vinyl acetate-ethylene copolymer, an ethylene-alpha olefin copolymer, a chlorinated polyethylene, etc. are mentioned, for example.

[0027] As a stabilization assistant which can be used with the polyvinyl chloride resin system constituent of this invention, the metal salts of an organic phosphorous-acid ester compound, an epoxy compound, an antioxidant, a tintion enhancement agent, a hindered amine light stabiliser, an ultraviolet ray absorbent, a metaled oxide, a hydroxide, and an organic acid etc. are mentioned, for example.

[0028] As an example of an organic phosphorous-acid ester compound A tris phenyl ***** fight, a tris nonylphenyl ***** fight, A diphenyl ***** fight, a ***** phenyl ***** fight, A tris ***** fight, a tris (2-ethylhexyl) ***** fight, A tris (dinonylphenyl) ***** fight, a tris (2, 4-G t-buthylphenyl) ***** fight, A 4 and 4'-isopropylidene diphenyl ***** fight, 2 and 2-methylene screw (4, 6-G t-buthylphenyl) octylphosphite, Cyclic neopentane tetraailbis (2, 4-G t-buthylphenyl ***** fight), A cyclic-neopentane-tetraailbis (2 or 6G t-butyl-4-methylphenyl) ***** fight, Cyclic neopentane tetraailbis (octadecyl ***** fight), ***** hydroxy ***** , a dinonylphenyl hydroxy ***** fight, etc. can be mentioned.

[0029] As an epoxy compound, it is the compound which has oxy-run oxygen in structure, for example, and the epoxy compound of the epoxy compound of animals-and-plants unsaturation fats and oils, such as epoxidation soybean oil and the epoxidation linseed oil, the epoxy compound of unsaturation fatty acid ester, aromatic series and aliphatic glycidyl ether, or a saturation alicyclic compound etc. is mentioned.

[0030] It is the sulfur-containing yellow system compound which has as an antioxidant the compound or thioether machine chosen out of the group which consists the phenolic group by which the hydroxy group was *****ed by at least one the third class or the second class alkyl group, for example of one piece or a compound which it has four pieces in the same molecule. As the example, a styrene-ized Parakou resol, 2, a 6-G tert-butyl-4-methyl phenol, Butyl-ized anisole, 4, and 4'-butylidenebis (6-tert-butyl 3-methyl phenol), A 2 and 2'-methylene screw (6-tert-butyl 4-methyl phenol), 1, 3, and 5-trimethyl -- 2, 4, and 6-tris (3 or 5G tert-butyl 4-hydroxy benzyl) benzene -- Tetrakis [3 - (4-hydroxy 3, 5-G tert-buthylphenyl) propionyl oxymethyl] methane, Phenol system compounds, such as n-octadecyl 3-(3', 5' - G tert-butyl 4'-hydroxyphenyl) propionate, Sulfur-containing yellow system compounds, such as dilauryl thiodipropionate, distearyl thiodipropionate, and pentaerythritol tetrakis (beta-laurylthio propionate), are mentioned.

[0031] As a hindered amine light stabiliser, the 2-methyl-2-(2, 2, 6, and 6-tetrapod-methyl-4-piperidyl) amino-N-(2, 2, 6, and 6-tetramethyl-4-piperidyl) ***** flax id, poly [(6-morpholino-S-triazine -2 and 4-**** [(2, 2, 6, and 6-tetramethyl-4-piperidyl) *****] hexamethylene [(2, 2, 6, and 6-tetramethyl-4-*****)] --) 6-(1, 1, 3, and 3-tetramethyl butylamino)-S-triazine -2 and poly [4-**** [(2, 2, 6, and 6-tetramethyl-4-piperidyl) *****] hexamethylene [(2, 2, 6, and 6-tetramethyl-4-*****)] --] -- Screw (2, 2, 6, and 6-tetramethyl-4-piperidyl) sebacate, Tetrapod (2, 2, 6, and 6-tetramethyl-4-piperidyl) - 1, 2, 3, 4-butanetetracarboxylate, The 2-[(2, 2, 6, and 6-tetramethyl-4-piperidyl) *****] 2-butyryl [(2, 2, 6, and 6-tetramethyl-4-*****)*****], A 2-(3, 5-G tert-butyl-4-hydroxy benzyl)-2-n-butyl malonic-acid screw (1, 2, 2, 6, and 6-pen reservoir chill-4-piperidyl) etc. is mentioned.

[0032] As an ultraviolet ray absorbent, a p-tert-buthylphenyl ***** rate, 2, 4 dihydroxy benzophenone, 2, and 2'-dihydroxy-4-methoxybenzophenone, The ethyl-2-cyano -3, 3'-diphenyl acrylate, the 2-ethylhexyl-2-cyano -3, 3'-diphenyl acrylate, A 2(2'-hydroxy-3' -tert-butyl -5'-methylphenyl)-5-***** benzotriazol, Two (2' - hydroxy-3', 5'-G tert-buthylphenyl) benzotriazol, Two (2' - hydroxy-5'-methylphenyl) benzotriazol, 2-hydroxy-4-methoxybenzophenone, a 2-hydroxy-5-***** benzophenone, A 2-hydroxy-4-octoxybenzophenone, two (2'-hydroxy-4-octoxy phenyl) benzotriazols, phenyl ***** rate, 2, 2', 4, and 4'-tetrapod hydroxy benzophenone etc. is mentioned.

[0033] As a metal salt as a thermostabilizer, the metal salt of an organic acid, a metaled oxide, a hydroxide, zeolites, and hydrotalcites are mentioned.

[0034] As a configuration organic acid of the metal salt of an organic acid, phenolss, such as a phenol, p-tert-butylphenol, and a nonyl phenol, are again mentioned for a propionic acid, a capric acid, 2 ethylhexyl acid, a neo octanoic acid, a decanoic acid, a myristic acid, an oleic acid, stearin acid, ricinoleic acid, 12-hydroxy stearin acid, an adipic acid, sebacic acid, a maleic acid, a benzoic acid, a toluic acid, a p-tert-butyl-benzoic acid, a salicylic acid, a phthalic acid, a thioglycolic acid, mercaptopropionic acid, a thiodipropionic acid As a metal to constitute, a lithium, sodium, magnesium, a potassium, calcium, aluminum, etc. are mentioned.

[0035] As a bulking agent which can be used with the polyvinyl chloride resin system constituent of this invention, a precipitated calcium carbonate, a whiting, clay, talc, a silica, ***** , a pumice powder, a mica powder, the alumina sulfuric-acid aluminum, a barium sulfate, a glass fiber, a carbon fiber, graphite, wood flour, etc. are mentioned, for example.

[0036] The polyvinyl chloride resin system constituent in this invention can use a general compounding agent, i.e., an antistatic agent, a foaming agent, a pigment, a fluorescence agent, a flame retarder, a release agent, an antibacterial agent, etc. in addition to the above.

[0037]

[Example] Hereafter, this invention is not limited by these although an example and the example of a comparison explain this invention concretely.

[0038] (Manufacture of a perchloric acid processing hydrotalcite) Using the ***** mizer 1 made from Consonance Chemical industry as hydrotalcites, perchloric acid processing was carried out according to the conventional method, and the predetermined quantity (20%, 50%, 60%, 90%) of the carbonic acid anion in the ***** mizer 1 was transposed to the perchloric acid anion (Table 1).

[0039]

[Table 1]

過塩素酸処理ハイト・ワルサイト類 $Mg_4Al_2(OH)_{12}(CO_3)_x(ClO_4)_{1-x} \cdot 3H_2O$

	X	Y
過塩素酸処理ハイト・ワルサイト 1	0.8	0.4
過塩素酸処理ハイト・ワルサイト 2	0.5	1.0
過塩素酸処理ハイト・ワルサイト 3	0.4	1.2
過塩素酸処理ハイト・ワルサイト 4	0.1	1.8

[0040] (Example 1) ***** during 3 minutes and the sheet were created with the 6 inch open roll which prepared the

following compound to 180 degreeC. The test piece of a suitable size was cut out from this sheet, it put into the gear oven aging tester set as 190 degreeC, and the heat instability test was performed. The sheet put into the gear oven aging tester was extracted for every predetermined time, measured delta E value to those standard white plates by the color analysis apparatus (COLOR ANALYZER TC-1800MK-II: product made from the Tokyo ****, Inc.), and made this the index of color tone change. The value of deltaE shows that a color tone is as good as the parvus.

[0041]

(Examination combination)

A polyvinyl chloride resin (P= 1050) 100 whittings 3calcium-St 0.5 ***** SL-02 (Riken Vitamin make) 0.5 diphenyl tridecyl phosphite 0.5DOP 5.0 stabilizing agents (Table 2)

[0042]

[Table 2]

実施例

	添加剤	未加 熱	1 0 分	2 0 分	3 0 分	4 0 分
比較例 1	なし	22.3	35.9	49.5	55.8	71.7
比較例 2	過塩素酸処理ハイトロタルサイト 3 0.3	21.4	33.1	45.5	46.8	50.2
比較例 3	ペンタエリトリール 0.3	25.5	38.3	52.1	63.4	75.6
比較例 4	ジトリメチロール・ロハ・ン 0.3	20.0	30.4	51.2	61.4	87.4
比較例 5	過塩素酸処理ハイトロタルサイト 3 0.3 ペンタエリトリール 0.3	21.1	29.6	40.1	45.5	49.8
比較例 6	過塩素酸処理ハイトロタルサイト 3 0.3 ジベンゾイルメタン 0.1	25.6	39.2	48.2	51.3	65.6
比較例 7	アルカマイザー 1 0.3 ジトリメチロール・ロハ・ン 0.3	34.7	43.5	60.1	72.9	89.9
実施例 1	過塩素酸処理ハイトロタルサイト 3 0.3 ジトリメチロール・ロハ・ン 0.1	19.9	27.8	29.2	27.6	33.1
実施例 2	過塩素酸処理ハイトロタルサイト 3 0.3 ジトリメチロール・ロハ・ン 0.3	19.4	23.3	25.2	26.7	32.3
実施例 3	過塩素酸処理ハイトロタルサイト 4 0.3 ジトリメチロール・ロハ・ン 0.3	18.9	22.5	23.7	25.5	26.4
実施例 4	過塩素酸処理ハイトロタルサイト 2 0.3 ジトリメチロール・ロハ・ン 0.3	19.5	26.6	28.8	29.1	35.1
実施例 5	過塩素酸処理ハイトロタルサイト 3 0.3 トリメチロール・ロハ・ン 0.3	19.3	22.3	27.9	33.2	38.6
実施例 6	過塩素酸処理ハイトロタルサイト 3 0.3 ジトリメチロール・ロハ・ン (M.W=約90 0) 0.3	20.2	29.8	35.2	37.3	39.5

[0043] When not using heavy metal, such as a zinc compound, a tin compound, and a lead compound, so that clearly from an example (example 1 of a comparison), even if tinction nature is remarkable and uses a perchloric acid processing hydrotalcite (example 2 of a comparison), or polyols (examples 3 and 4 of a comparison) for this, the effect does not almost exist and is inadequate. Even if it uses together both perchloric acid processing hydrotalcite and pentaerythritol (example 5 of a comparison), the effect is completely insufficient.

[0044] Moreover, even if it uses a hydrotalcite and a dibenzoylmethane together, the tinction improvement effect hardly accepts (example 7 of a comparison).

[0045] On the other hand, when the ***** roll compounds expressed with the perchloric acid processing hydrotalcite expressed with the above-ization 1 concerning this invention and the above-ization 2 are used together and used (examples 1-6), the improvement effect of the tinction nature of the heat history is remarkable.

[0046] [Effect of the Invention] The polyvinyl chloride resin constituent by this invention is excellent in heat tinction nature, and can be used suitable for all intended use. It can be used suitable for distributing water pipes, such as a semiconductor manufacturing facility which dislikes contamination especially by heavy metal, etc.

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TECHNICAL PROBLEM

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Effect

[Effect of the Invention] The polyvinyl chloride resin constituent by this invention is excellent in heat tinction nature, and can be used suitable for all intended use. It can be used suitable for distributing water pipes, such as a semiconductor manufacturing facility which dislikes contamination especially by heavy metal, etc.

[Translation done.]

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Technique

[Description of the Prior Art] To heat and light, a polyvinyl chloride resin is an unstable resin and tends to cause a tinction degradation by the pyrolysis which mainly originated in the dehydrochlorination especially at the time of a fabricating operation. Addition of a stabilizer is made into **s for elimination of the degradation factor by the heat at the time of this fabricating operation etc., or reduction-izing.

[0003] Conventionally, stabilizers, such as compound metallic-soap systems, such as a lead system, and Ba, Zn, calcium, and an organic tin system, are used, and further, an epoxy compound, the organic phosphorous-acid ester compound, beta-diketone compound, the polyhydric-alcohol compound, the nitrogen-containing compound, etc. used together, and have been used.

[0004] It is increasing, when used for the intended use which the intended use of PVC is expanded and dislikes contamination by heavy metal; such as a semiconductor industrial facility relation and a food-stuff-industry facility relation, to a degree very much in recent years.

[0005] For example, in semiconductor manufacturing facility relations (a cleaning equipment, etching system, etc.), the various processings in process must be carried out, it will be in process, these metals will be eluted, and the polyvinyl chloride resin which contains heavy metal compounds, such as Pb, Sn, and Zn, as a stabilizer will affect electronic parts etc. For this reason, not to contain heavy metal is desired in the resin constituent for semiconductor manufacturing facilities.

[0006] conventionally, the tubing material used for ultrapure-water piping for plants etc. lessens irregularity of an inside-a-hall side as much as possible, and obtains a smooth front face -- as -- manipulation speed -- dropping -- metal mold -- inner pass time -- more than twice -- it is applying and fabricating Therefore, in response to the heat history, it becomes easy to disassemble a resin. Moreover, since a productivity is also very bad, the study in a combination side is performed.

[0007] Moreover, although it is indicated conventionally that combined use of **ized alcohol, dihydroxy pyridines, or beta-amino crotonic-acid ester adds an amino carboxylic acid to JP,62-197439,A as non-metal combination at JP,62-273243,A, in the above-mentioned non-metal resin constituent, the heat stabilization of any cannot fully be carried out, but it is easy to color them.

[0008] Moreover, the vinyl-chloride-resin constituent which JP,7-278389,A is made to contain so that the proportion of the perchloric acid anion to a carbonic acid anion may become a 1.6-30wt time, and becomes, and is characterized by Zn salt of an organic acid, Cd salt, Pb salt, and not carrying out organic Sn compound inclusion is indicated. However, even if it bore the powder slush molding which there is much plasticizer and is blended, like a pipe and a hard variant article, since high shearing force was applied, it was easy to color and was inadequate [the above-mentioned constituent / the heat history was large, and] in non-plastic or extrusion molding with little plasticizer, practical.

[0009] Moreover, if zinc compounds, such as a zinc stearate, are not used together as illustrated by the example although the chlorination vinyl-polymer constituent with which 5-15, and the number of hydroxyl groups are characterized [a ditrimethylol propane and a carbon atomic number] by consisting of the combination with the polyol below 100 degreeC by the melting point by 2-10 is indicated by JP,57-151637,A, tinction is remarkable, and good mold goods were not obtained. Moreover, although the stabilizing agent which comes to contain zinc soap and ***** rolls in JP,9-151288,A was indicated, it was ineffective and combined use of zinc soap was [a ***** rolls independent] indispensable.

[0010] Moreover, although adding the partial ester and the halogen oxygen-acid salt of the metal salt of an organic acid and **ized alcohol was indicated by JP,58-127751.A, if each example was using Zn compound together and did not use Zn compound together, a good hue was not acquired but it was inadequate.

[Translation done.]

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MEANS

[Means for Solving the Problem] As a result of this invention person's etc. repeating a study zealously in view of such status, by combining the condensate of (a) perchloric acid processing hydrotalcite compound, (b) ***** roll compounds, and/or ***** roll compounds, excluding heavy metal compounds, such as Zn compound, Cd compound, Ba compound, Pb compound, and Sn compound, it found out that the polyvinyl chloride resin system constituent which is excellent in the thermal resistance with a good hue was obtained, and ** also reached this invention.

[0013]

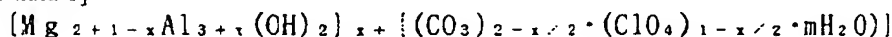
[Embodiments of the Invention] Hereafter, this invention is explained in detail. The stabilizing agent of this invention A polyvinyl chloride resin, for example, the homopolymer of a vinyl chloride, The copolymer which makes a vinyl chloride a principal component, a chlorinated polyethylene, a polyvinylidene chloride, As opposed to the mixture (polymer blend) of chlorination polypropylene, these mixtures or the above-mentioned polymer, and other polymers etc. It is the stabilizing agent which can give the thermal resistance which did not blend heavy metal compounds, such as Zn compound, Cd compound, Ba compound, Pb compound, and Sn compound, but was excellent also in **. Perchloric acid processing hydrotalcite compounds It is characterized by containing at least one or more sorts chosen out of the condensate of ***** roll compounds and/or those ***** roll compounds.

[0014] As a polyvinyl chloride resin used with the polyvinyl chloride resin system constituent of this invention, it is the mixture (polymer blend) of the homopolymer of a vinyl chloride, the copolymer which makes a vinyl chloride a principal component, a chlorinated polyethylene, a polyvinylidene chloride, chlorination polypropylene, these mixtures or the above-mentioned polymer, and other polymers etc., for example. Specifically, they are a polyvinyl chloride and vinyl acetate-vinyl chloride copolymer, an ethylene-vinyl chloride copolymer, a propylene-vinyl chloride copolymer, an ethylene-vinyl acetate-vinyl chloride copolymer, an acrylic-ester-vinyl chloride copolymer, etc. As an example of the polymer which does not contain a vinyl chloride, they are an ethylene-vinyl acetate copolymer, an ethylene-vinyl acetate-1 carbon-monoxide copolymer, an acrylic-ester polymer, a meta-acrylic ester-butadiene-styrene graft copolymer, or a special polyurethane resin.

[0015] Moreover, as perchloric acid processing hydrotalcite compounds used by this invention, the stratified compound shown, for example by ** 1 is mentioned.

[0016]

[Formula 1]



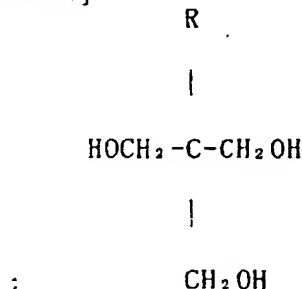
(式中 m は正の数を、x は 0.33 以下の正の数を表す)

[0017] moreover -- addition number of copies of the perchloric acid processing hydrotalcite compounds used by this invention ***** -- the polyvinyl chloride resin 100 weight section -- receiving -- 0.01 to 5 weight section -- it is preferably used in the domain of 0.03 to 3 weight section The effect over a thermal stability is scarce, and even if it uses it exceeding 5 weight section, it is deficient in the increase-in-quantity effect at less than 0.01.

[0018] Moreover, the ***** roll compounds used by this invention are shown by ** 2, and a monomer and/or its condensation product are mentioned.

[0019]

[Formula 2]



上記一般式 (2) において、R は炭素数 1 以上のアルキル基等の

有機残基を示す。

[0020] As an example of ***** roll compounds and the condensate of those, ***** roll ethane, a trimethylol propane, ***** roll butane, a ***** roll hexane, a ***** roll octane, ditrimethylol ethane, a ditrimethylol propane, a ditrimethylol hexane, a tris trimethylol propane, a poly-trimethylol propane, etc. are mentioned.

[0021] moreover -- the ***** roll compounds used by this invention, and addition number of copies of the condensate ***** -- the polyvinyl chloride resin 100 weight section -- receiving -- 0.01 to 5 weight section -- it is

preferably used in the domain of 0.03 to 3 weight section The effect over a thermal stability is scarce, and even if it uses it exceeding 5 weight section, it is deficient in the increase-in-quantity effect at less than 0.01.

[0022] The polyvinyl chloride resin in this invention can be made to contain the various additives usually used in the domain which does not spoil the effect of this invention. It is not the object limited especially as an additive. For example, a plasticizer, a lubricant, processing aid, a reinforcement and a stabilization assistant (organic phosphite, an epoxy compound, and an antioxidant --) The flame retarder as functional grant agents, such as a diketone and perchloric acid salts, an antistatic agent, Although the metallic oxide as a pigment, a metal complex compound, a metal-containing pigment, etc. are mentioned further, the metal salts which do not contain the heavy metal as an ultraviolet ray absorbent, a light stabilizer, a foaming agent, and a thermostabilizer, the inorganic compound as a bulking agent, and the thing which does not contain heavy metal are desirable.

[0023] As a plasticizer which can be used with the polyvinyl chloride resin system constituent of this invention, epoxy compounds, such as dialkyl free-wheel-plate rates, dialkyl horse mackerel peats, dialkyl sebacate, polyester system plasticizers that make an adipic acid a principal component, organic phosphoric ester, chlorinated paraffin and epoxidation soybean oil, and the epoxidation linseed oil, are mentioned, for example.

[0024] As a lubricant which can be used with the polyvinyl chloride resin system constituent of this invention, the paraffine-wax, liquid paraffin, polyethylene wax, polypropylene wax, montanoic-acid wax, higher-fatty-acid, high-class fatty-alcohol, and fatty-acid flax id, fatty acid ester, etc. are mentioned, for example.

[0025] As processing aid which can be used with the polyvinyl chloride resin system constituent of this invention, that which has mainly been entitled, for example by tradenames, such as the money ace of Kanegafuchi Chemical Industry Co., Ltd. of an acrylic resin, meta-***** of Mitsubishi Rayon Co., Ltd., and Palaloid of Kureha Chemical Industry Co., Ltd., is mentioned.

[0026] As a reinforcement which can be used with the polyvinyl chloride resin system constituent of this invention, an acrylonitrile-styrene-butadiene-rubber resin, a methylmetaacrylate-styrene-butadiene-rubber resin, an acrylic resin, butadiene resins, a vinyl acetate-ethylene copolymer, an ethylene-alpha olefin copolymer, a chlorinated polyethylene, etc. are mentioned, for example.

[0027] As a stabilization assistant which can be used with the polyvinyl chloride resin system constituent of this invention, the metal salts of an organic phosphorous-acid ester compound, an epoxy compound, an antioxidant, a tinction enhancement agent, a hindered amine light stabiliser, an ultraviolet ray absorbent, a metaled oxide, a hydroxide, and an organic acid etc. are mentioned, for example.

[0028] As an example of an organic phosphorous-acid ester compound A tris phenyl ***** fight, a tris nonylphenyl ***** fight, A diphenyl ***** fight, a ***** phenyl ***** fight, A tris ***** fight, a tris (2-ethylhexyl) ***** fight, A tris (dinonylphenyl) ***** fight, a tris (2, 4-G t-buthylphenyl) ***** fight, A 4 and 4'-isopropylidene diphenyl ***** fight, 2 and 2-methylene screw (4, 6-G t-buthylphenyl) octylphosphite, Cyclic neopentane tetraailbis (2, 4-G t-buthylphenyl ***** fight), A cyclic-neopentane-tetraailbis (2 or 6G t-butyl-4-methylphenyl) ***** fight, Cyclic neopentane tetraailbis (octadecyl ***** fight), ***** hydroxy ***** , a dinonylphenyl hydroxy ***** fight, etc. can be mentioned.

[0029] As an epoxy compound, it is the compound which has oxy-run oxygen in structure, for example, and the epoxy compound of the epoxy compound of animals-and-plants unsaturation fats and oils, such as epoxidation soybean oil and the epoxidation linseed oil, the epoxy compound of unsaturation fatty acid ester, aromatic series and aliphatic glycidyl ether, or a saturation alicyclic compound etc. is mentioned.

[0030] It is the sulfur-containing yellow system compound which has as an antioxidant the compound or thioether machine chosen out of the group which consists the phenolic group by which the hydroxy group was *****ed by at least one the third class or the second class alkyl group, for example of one piece or a compound which it has four pieces in the same molecule. As the example, a styrene-ized Parakou resol, 2, a 6-G tert-butyl-4-methyl phenol, Butyl-ized anisole, 4, and 4'-butylidenebis (6-tert-butyl 3-methyl phenol), A 2 and 2'-methylene screw (6-tert-butyl 4-methyl phenol), 1, 3, and 5-trimethyl -- 2, 4, and 6-tris (3 or 5G tert-butyl 4-hydroxy benzyl) benzene -- Tetrakis [3 - (4-hydroxy 3, 5-G tert-buthylphenyl) propionyl oxymethyl] methane, Phenol system compounds, such as n-octadecyl 3-(3', 5' - G tert-butyl 4'-hydroxyphenyl) propionate, Sulfur-containing yellow system compounds, such as dilauryl thiodipropionate, distearyl thiodipropionate, and pentaerythritol tetrakis (beta-laurylthio propionate), are mentioned.

[0031] As a hindered amine light stabiliser, the 2-methyl-2-(2, 2, 6, and 6-tetrapod-methyl-4-piperidyl) amino-N-(2, 2, 6, and 6-tetramethyl-4-piperidyl) ***** flax id, poly [(6-morpholino-S-triazine -2 and 4-**** [(2, 2, 6, and 6-tetramethyl-4-piperidyl) *****] hexamethylene [(2, 2, 6, and 6-tetramethyl-4-*****)] --) 6-(1, 1, 3, and 3-tetramethyl butylamino)-S-triazine -2 and poly [4-**** [(2, 2, 6, and 6-tetramethyl-4-piperidyl) *****] hexamethylene [(2, 2, 6, and 6-tetramethyl-4-*****)] --) -- Screw (2, 2, 6, and 6-tetramethyl-4-piperidyl) sebacate, Tetrapod (2, 2, 6, and 6-tetramethyl-4-piperidyl) - 1, 2, 3, 4-butanetetraacboxylate, The 2-[(2, 2, 6, and 6-tetramethyl-4-piperidyl) *****] 2-butyryl [(2, 2, 6, and 6-tetramethyl-4-*****) *****], A 2-(3, 5-G tert-butyl-4-hydroxy benzyl)-2-n-butyl malonic-acid screw (1, 2, 2, 6, and 6-pen reservoir chill-4-piperidyl) etc. is mentioned.

[0032] As an ultraviolet ray absorbent, a p-tert-buthylphenyl ***** rate, 2, 4 dihydroxy benzophenone, 2, and 2'-dihydroxy-4-methoxybenzophenone, The ethyl-2-cyano -3, 3'-diphenyl acrylate, the 2-ethylhexyl-2-cyano -3, 3'-diphenyl acrylate, A 2(2'-hydroxy-3' -tert-butyl -5'-methylphenyl)-5-***** benzotriazol, Two (2' - hydroxy-3', 5'-G tert-buthylphenyl) benzotriazol, Two (2' - hydroxy-5'-methylphenyl) benzotriazol, 2-hydroxy-4-methoxybenzophenone, a 2-hydroxy-5-***** benzophenone, A 2-hydroxy-4-octoxybenzophenone, two (2'-hydroxy-4-octoxy phenyl) benzotriazols, phenyl ***** rate, 2, 2', 4, and 4'-tetrapod hydroxy benzophenone etc. is mentioned.

[0033] As a metal salt as a thermostabilizer, the metal salt of an organic acid, a metaled oxide, a hydroxide, zeolites, and hydrotalcites are mentioned.

[0034] As a configuration organic acid of the metal salt of an organic acid, phenolss, such as a phenol, p-tert-butylphenol, and a nonyl phenol, are again mentioned for a propionic acid, a capric acid, 2 ethylhexyl acid, a neo octanoic acid, a decanoic acid, a myristic acid, an oleic acid, stearin acid, ricinoleic acid, 12-hydroxy stearin acid, an adipic acid, sebacic acid, a maleic acid, a benzoic acid, a toluic acid, a p-tert-butyl-benzoic acid, a salicylic acid, a phthalic acid, a thioglycolic acid, mercaptopropionic acid, a thiodipropionic acid As a metal to constitute, a lithium, sodium, magnesium, a potassium, calcium, aluminum, etc. are mentioned.

[0035] As a bulking agent which can be used with the polyvinyl chloride resin system constituent of this invention, a precipitated calcium carbonate, a whiting, clay, talc, a silica, ***** , a pumice powder, a mica powder, the alumina

sulfuric-acid aluminum, a barium sulfate, a glass fiber, a carbon fiber, graphite, wood flour, etc. are mentioned, for example.

[0036] The polyvinyl chloride resin system constituent in this invention can use a general compounding agent, i.e., an antistatic agent, a foaming agent, a pigment, a fluorescence agent, a flame retarder, a release agent, an antibacterial agent, etc. in addition to the above.

[Translation done.]

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EXAMPLE

[Example] Hereafter, this invention is not limited by these although an example and the example of a comparison explain this invention concretely.

[0038] (Manufacture of a perchloric acid processing hydrotalcite) Using the ***** mizer 1 made from Consonance Chemical industry as hydrotalcites, perchloric acid processing was carried out according to the conventional method, and the predetermined quantity (20%, 50%, 60%, 90%) of the carbonic acid anion in the ***** mizer 1 was transposed to the perchloric acid anion (Table 1).

[0039]

[Table 1]

過塩素酸処理ハイトロタルサイト類 $Mg_3Al_2(OH)_2(CO_3)_1(ClO_4)_1 \cdot 3H_2O$

	X	Y
過塩素酸処理ハイトロタルサイト 1	0.8	0.4
過塩素酸処理ハイトロタルサイト 2	0.5	1.0
過塩素酸処理ハイトロタルサイト 3	0.4	1.2
過塩素酸処理ハイトロタルサイト 4	0.1	1.8

[0040] (Example 1) ***** during 3 minutes and the sheet were created with the 6 inch open roll which prepared the following compound to 180 degreeC. The test piece of a suitable size was cut out from this sheet, it put into the gear oven aging tester set as 190 degreeC, and the heat instability test was performed. The sheet put into the gear oven aging tester was extracted for every predetermined time, measured delta E value to those standard white plates by the color analysis apparatus (COLOR ANALYZER TC-1800MK- II: product made from the Tokyo ****, Inc.), and made this the index of color tone change. The value of deltaE shows that a color tone is as good as the parvus.

[0041]

(Examination combination)

A polyvinyl chloride resin (P= 1050) 100 whittings 3calcium-St 0.5 ***** SL-02 (Riken Vitamin make) 0.5 diphenyl tridecyl phosphite 0.5DOP 5.0 stabilizing agents (Table 2)

[0042]

[Table 2]

実施例

	添加剤	未加 熱	10 分	20 分	30 分	40 分
比較例 1	なし	22.3	35.9	49.5	55.8	71.7
比較例 2	過塩素酸処理ハイト・ロタルサイト3 0.3	21.4	33.1	45.5	46.8	50.2
比較例 3	ペンタエリスリトール 0.3	25.5	38.3	62.1	63.4	75.6
比較例 4	ジ・トリメチロール・ロハ・ン 0.3	20.0	30.4	51.2	61.4	87.4
比較例 5	過塩素酸処理ハイト・ロタルサイト3 0.3 ペンタエリスリトール 0.3	21.1	29.6	40.1	45.5	49.8
比較例 6	過塩素酸処理ハイト・ロタルサイト3 0.3 ジベンゾイルメタン 0.1	25.6	39.2	48.2	51.3	65.6
比較例 7	アルカマイザー1 0.3 ジ・トリメチロール・ロハ・ン 0.3	34.7	43.5	60.1	72.9	89.9
実施例 1	過塩素酸処理ハイト・ロタルサイト3 0.3 ジ・トリメチロール・ロハ・ン 0.1	19.9	27.8	29.2	27.6	33.1
実施例 2	過塩素酸処理ハイト・ロタルサイト3 0.3 ジ・トリメチロール・ロハ・ン 0.3	19.4	23.3	25.2	26.7	32.3
実施例 3	過塩素酸処理ハイト・ロタルサイト4 0.3 ジ・トリメチロール・ロハ・ン 0.3	18.9	22.5	23.7	25.5	26.4
実施例 4	過塩素酸処理ハイト・ロタルサイト2 0.3 ジ・トリメチロール・ロハ・ン 0.3	19.5	26.6	28.8	29.1	35.1
実施例 5	過塩素酸処理ハイト・ロタルサイト3 0.3 トリメチロール・ロハ・ン 0.3	19.3	22.3	27.9	33.2	38.6
実施例 6	過塩素酸処理ハイト・ロタルサイト3 0.3 オ・リトリメチロール・ロハ・ン (M.W=約90 0) 0.3	20.2	29.8	35.2	37.3	39.5

[0043] When not using heavy metal, such as a zinc compound, a tin compound, and a lead compound, so that clearly from an example (example 1 of a comparison), even if tincture nature is remarkable and uses a perchloric acid processing hydrotalcite (example 2 of a comparison), or polyols (examples 3 and 4 of a comparison) for this, the effect does not almost exist and is inadequate. Even if it uses together both perchloric acid processing hydrotalcite and pentaerythritol (example 5 of a comparison), the effect is completely insufficient.

[0044] Moreover, even if it uses a hydrotalcite and a dibenzoylmethane together, the tincture improvement effect hardly accepts (example 7 of a comparison).

[0045] On the other hand, when the ***** roll compounds expressed with the perchloric acid processing hydrotalcite expressed with the above-ization 1 concerning this invention and the above-ization 2 are used together and used (examples 1-6), the improvement effect of the tincture nature of the heat history is remarkable.

[Translation done.]

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DE286 E0057 F0076 F0020

F0038 F0037 F0040 F0050

F0060 F0070 F0170

(54) 【発明の名称】 ポリ塩化ビニル樹脂用安定化剤及びポリ塩化ビニル樹脂系組成物

(57) 【要約】

【課題】 重金属を実質上含まない、熱安定性の良好なポリ塩化ビニル樹脂用安定化剤及びポリ塩化ビニル樹脂系組成物提供する。

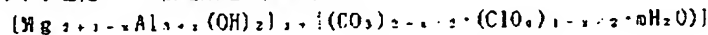
【解決手段】 過塩素酸処理ハイドロタルサイト化合物類とトリメチロール化合物類及び／またはトリメチロール化合物類の縮合物の1種以上からなり、且つ、Zn, Cd, Ba, Sn, Pb等の重金属を実質上含まないポリ塩化ビニル樹脂用安定化剤及びポリ塩化ビニル樹脂系組成物。

類及び/またはトリメチロール化合物類の縮合物とを組み合わせることによって Zn 化合物、Cd 化合物、Ba 化合物、Pb 化合物、Sn 化合物等の重金属化合物を含まずとも色相の良好な、耐熱性に優れたポリ塩化ビニル樹脂系組成物が得られることを見出し、本発明に到達した。

【0013】

【発明の実施の形態】以下、本発明を詳細に説明する。本発明の安定化剤はポリ塩化ビニル樹脂、例えば塩化ビニルの単一重合体、塩化ビニルを主成分とする共重合体、塩素化ポリエチレン、ポリ塩化ビニリデン、塩素化ポリプロピレン、これらの混合体、又は上記重合体と他の重合体との混合体（ポリマーブレンド）等に対し、Zn 化合物、Cd 化合物、Ba 化合物、Pb 化合物、Sn 化合物等の重金属化合物を配合せずとも優れた耐熱性を付与する安定化剤であり、過塩素酸処理ハイドロタルサイト化合物類と、トリメチロール化合物類及び/またはそれらのトリメチロール化合物類の縮合物から選ばれた少なくとも1種以上を含有することを特徴とする。

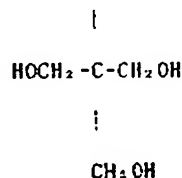
【0014】本発明のポリ塩化ビニル樹脂系組成物で用*20



（式中 m は正の数を、x は 0.33 以下の正の数を表す）

【0017】また本発明で使用する過塩素酸処理ハイドロタルサイト化合物類の添加部数としてはポリ塩化ビニル樹脂100重量部に対し0.01から5重量部、好ましくは0.03から3重量部の範囲で使用する。0.01未満では熱安定性に対する効果が乏しく、5重量部を超えて使用しても、増量効果に乏しい。

R



上記一般式（2）において、Rは炭素数1以上のアルキル基等の

有機残基を示す。

【0020】トリメチロール化合物類及びその縮合物の具体例としてはトリメチロールエタン、トリメチロールプロパン、トリメチロールブタン、トリメチロールヘキサン、トリメチロールオクタン、ジトリメチロールエタン、ジトリメチロールプロパン、ジトリメチロールヘキサン、トリストリメチロールプロパン、ポリトリメチロールプロパン等が挙げられる。

【0021】また本発明で使用するトリメチロール化合物類及びその縮合物の添加部数としてはポリ塩化ビニル樹脂100重量部に対し0.01から5重量部、好ま

*いられるポリ塩化ビニル樹脂としては、例えば塩化ビニルの単一重合体、塩化ビニルを主成分とする共重合体、塩素化ポリエチレン、ポリ塩化ビニリデン、塩素化ポリプロピレン、これらの混合体、又は上記重合体と他の重合体との混合体（ポリマーブレンド）等である。具体的にはポリ塩化ビニル、酢酸ビニル-塩化ビニル共重合体、エチレン-塩化ビニル共重合体、プロピレン-塩化ビニル共重合体、エチレン-酢酸ビニル-塩化ビニル共重合体、アクリル酸エステル-塩化ビニル共重合体等である。塩化ビニルを含まない重合体の例として、エチレン-酢酸ビニル共重合体、エチレン-酢酸ビニル-酸化炭素共重合体、アクリル酸エステル重合体、メタアクリル酸エステル-ブタジエン-スチレングラフト共重合体、あるいは特殊ポリウレタン樹脂等である。

【0015】また本発明で使用する過塩素酸処理ハイドロタルサイト化合物類としては、例えば化1で示される層状化合物が挙げられる。

【0016】

【化1】

※【0018】また本発明で使用するトリメチロール化合物類は化2で示される単量体及び/またはその縮合物が挙げられる。

【0019】

【化2】

しくは0.03から3重量部の範囲で使用する。0.01未満では熱安定性に対する効果が乏しく、5重量部を超えて使用しても、増量効果に乏しい。

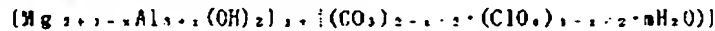
【0022】本発明におけるポリ塩化ビニル樹脂には、本発明の効果を損なわない範囲で通常使用されている種々の添加剤を含有させることができる。添加剤としては特に限定される物ではなく、例えば可塑剤、滑剤、加工助剤、強化剤、安定化助剤（有機亜リン酸塩類、エポキシ化合物、酸化防止剤、ジケトン、過塩素酸塩類等）、機能付与剤としての難燃剤、帯電防止剤、紫外線吸収

類及び／またはトリメチロール化合物類の縮合物とを組み合わせることによって Zn 化合物、Cd 化合物、Ba 化合物、Pb 化合物、Sn 化合物等の重金屬化合物を含まずとも色相の良好な、耐熱性に優れたポリ塩化ビニル樹脂系組成物が得られることを見出し、本発明に到達した。

【0013】

【発明の実施の形態】以下、本発明を詳細に説明する。本発明の安定化剤はポリ塩化ビニル樹脂、例えば塩化ビニルの単一重合体、塩化ビニルを主成分とする共重合体、塩素化ポリエチレン、ポリ塩化ビニリデン、塩素化ポリプロピレン、これらの混合体、又は上記重合体と他の重合体との混合体（ポリマーブレンド）等に対し、Zn 化合物、Cd 化合物、Ba 化合物、Pb 化合物、Sn 化合物等の重金屬化合物を配合せずとも優れた耐熱性を付与する安定化剤であり、過塩素酸処理ハイドロタルサイト化合物類と、トリメチロール化合物類及び／またはそれらのトリメチロール化合物類の縮合物から選ばれた少なくとも1種以上を含有することを特徴とする。

【0014】本発明のポリ塩化ビニル樹脂系組成物で用*20



（式中 m は正の数を、x は 0.33 以下の正の数を表す）

【0017】また本発明で使用する過塩素酸処理ハイドロタルサイト化合物類の添加部数としてはポリ塩化ビニル樹脂100重量部に対し0.01から5重量部、好ましくは0.03から3重量部の範囲で使用する。0.01未満では熱安定性に対する効果が乏しく、5重量部を越えて使用しても、増量効果に乏しい。

*いられるポリ塩化ビニル樹脂としては、例えば塩化ビニルの単一重合体、塩化ビニルを主成分とする共重合体、塩素化ポリエチレン、ポリ塩化ビニリデン、塩素化ポリプロピレン、これらの混合体、又は上記重合体と他の重合体との混合体（ポリマーブレンド）等である。具体的にはポリ塩化ビニル、酢酸ビニル-塩化ビニル共重合体、エチレン-塩化ビニル共重合体、プロピレン-塩化ビニル共重合体、エチレン-酢酸ビニル-塩化ビニル共重合体、アクリル酸エステル-塩化ビニル共重合体等である。塩化ビニルを含まない重合体の例としてエチレン-酢酸ビニル共重合体、エチレン-酢酸ビニル-酸化炭素共重合体、アクリル酸エステル重合体、メタアクリル酸エステル-ブタジエン-スチレングラフト共重合体、あるいは特殊ポリウレタン樹脂等である。

【0015】また本発明で使用する過塩素酸処理ハイドロタルサイト化合物類としては、例えば化1で示される層状化合物が挙げられる。

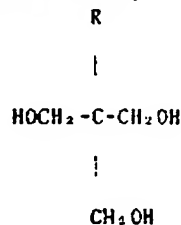
【0016】

【化1】

※【0018】また本発明で使用するトリメチロール化合物類は化2で示される単量体及び／またはその縮合物が挙げられる。

【0019】

【化2】



上記一般式（2）において、R は炭素数1以上のアルキル基等の

有機残基を示す。

【0020】トリメチロール化合物類及びその縮合物の具体例としてはトリメチロールエタン、トリメチロールプロパン、トリメチロールブタン、トリメチロールヘキサン、トリメチロールオクタン、ジトリメチロールエタン、ジトリメチロールプロパン、ジトリメチロールヘキサン、トリストリメチロールプロパン、ポリトリメチロールプロパン等が挙げられる。

【0021】また本発明で使用するトリメチロール化合物類及びその縮合物の添加部数としてはポリ塩化ビニル樹脂100重量部に対し0.01から5重量部、好ま

しくは0.03から3重量部の範囲で使用する。0.01未満では熱安定性に対する効果が乏しく、5重量部を越えて使用しても、増量効果に乏しい。

【0022】本発明におけるポリ塩化ビニル樹脂には、本発明の効果を損なわない範囲で通常使用されている種々の添加剤を含有させることができる。添加剤としては特に限定される物ではなく、例えば可塑剤、滑剤、加工助剤、強化剤、安定化助剤（有機亜リン酸塩類、エポキシ化合物、酸化防止剤、ジケトン、過塩素酸塩類等）、機能付与剤としての難燃剤、帯電防止剤、紫外線吸収

剤、光安定剤、発泡剤、熱安定剤としての重金屬を含まない金屬塩類、充填剤としての無機化合物、さらに顔料としての金屬酸化物、金屬錯化合物、含金屬顔料等が挙げられるが重金屬を含まないものが好ましい。

【0023】本発明のポリ塩化ビニル樹脂系組成物で使用する可塑剤としては、例えばジアルキルフタレート類、ジアルキルアジペート類、ジアルキルセバケート類、アジピン酸を主成分とするポリエステル系可塑剤類、有機リン酸エステル類、塩素化パラフィン類及びエポキシ化大豆油、エポキシ化アマニ油等のエポキシ化合物類が挙げられる。

【0024】本発明のポリ塩化ビニル樹脂系組成物で使用する滑剤としては、例えばパラフィンワックス、流動パラフィン、ポリエチレンワックス、ポリプロピレンワックス、モンタン酸ワックス、高級脂肪酸、高級脂肪酸アルコール、脂肪酸アミド、脂肪酸エステル等が挙げられる。

【0025】本発明のポリ塩化ビニル樹脂系組成物で使用する加工助剤としては、例えば主としてアクリル系樹脂の旭硝子化学工業（株）のカネエース、三菱レイヨン（株）のメタブレン、興羽化学工業（株）のパラロイド等の商品名が冠されているものが挙げられる。

【0026】本発明のポリ塩化ビニル樹脂系組成物で使用する強化剤としては、例えばアクリロニトリル-ブタジエン-スチレン樹脂、メチルメタアクリレート-ブタジエン-スチレン樹脂、アクリル系樹脂、ブタジエン樹脂、酢酸ビニル-エチレン共重合体、エチレン- α -オレフィン共重合体、塩素化ポリエチレン等が挙げられる。

【0027】本発明のポリ塩化ビニル樹脂系組成物で使用する安定化助剤としては、例えば有機亜リン酸エステル化合物、エポキシ化合物、酸化防止剤、着色改良剤、ヒンダードアミン系光安定剤、紫外線吸収剤、金属の酸化物、水酸化物、有機酸の金属塩類等が挙げられる。

【0028】有機亜リン酸エステル化合物の具体例としては、トリスフェニルフォスファイト、トリスノニルフェニルフォスファイト、ジフェニルデシルフォスファイト、ジトリデシルフェニルフォスファイト、トリスデシルフォスファイト、トリス（2-エチルヘキシル）フォスファイト、トリス（ジノニルフェニル）フォスファイト、トリス（2,4-ジ-*tert*-ブチルフェニル）フォスファイト、4,4'-イソプロピリデンジフェニルテトラアルキルフォスファイト、2,2-メチレンビス（4,6-ジ-*tert*-ブチルフェニル）オクチルホスファイト、サイクリックネオペンタンテトライルビス（2,4-ジ-*tert*-ブチルフェニル）フォスファイト、サイクリックネオペンタンテトライルビス（2,6-ジ-*tert*-ブチル-4-メチルフェニル）フォスファイト、サイクリックネオペンタンテトライルビス（オクタデシルフォス

ファイト）、フェニルデシルヒドロキシフォスファイト、ジノニルフェニルヒドロキシフォスファイト等を挙げることが出来る。

【0029】エポキシ化合物としては、例えばオキシラン酸素を構造中に持つ化合物で、エポキシ化大豆油、エポキシ化アマニ油等の助植物不飽和油脂のエポキシ化合物、不飽和脂肪酸エステルのエポキシ化合物、芳香族及び脂肪族のグリシジルエーテルあるいは飽和脂環化合物のエポキシ化合物等が挙げられる。

【0030】酸化防止剤としては、例えばヒドロキシ基が少なくとも1個の三級あるいは二級アルキル基によりヒンダードされたフェノール基を同一分子内に1個ないし4個持つ化合物からなる群から選ばれた化合物あるいはチオエーテル基を持つ含硫黄系化合物で、その具体例としてスチレン化パラクレゾール、2,6-ジ-*tert*-ブチル-4-メチルフェノール、ブチル化アニソール、4,4'-ブチリデンビス（6-*tert*-ブチル-3-メチルフェノール）、2,2'-メチレンビス（6-*tert*-ブチル-4-メチルフェノール）、1,3,5-トリメチル-2,4,6-トリス（3,5-ジ-*tert*-ブチル-4-ヒドロキシベンジル）ベンゼン、テトラキス〔3-（4-ヒドロキシ-3,5-ジ-*tert*-ブチルフェニル）プロピオニルオキシメチル〕メタン、*n*-オクタデシル-3-（3',5'-ジ-*tert*-ブチル-4'-ヒドロキシフェニル）プロピオネート等のフェノール系化合物、ジラウリルチオジプロピオネート、ジステアリルチオジプロピオネート、ペンタエリスリトールテトラキス（ β -ラウリルチオプロピオネート）等の含硫黄系化合物が挙げられる。

【0031】ヒンダードアミン系光安定剤としては、2-メチル-2-（2,2,6,6-テトラ-メチル-4-ビペリジル）アミノ-N-（2,2,6,6-テトラメチル-4-ビペリジル）プロピオアミド、ポリ〔（6-モルホリノ-S-トリアジン-2,4-ジル〔（2,2,6,6-テトラメチル-4-ビペリジル）イミノ〕ヘキサメチレン〔（2,2,6,6-テトラメチル-4-ビペリジル）イミノ〕〕、ポリ〔6-（1,1,3,3-テトラメチルブチルアミノ）-S-トリアジン-2,4-ジル〕〔（2,2,6,6-テトラメチル-4-ビペリジル）イミノ〕ヘキサメチレン〔（2,2,6,6-テトラメチル-4-ビペリジル）イミノ〕〕、ビス（2,2,6,6-テトラメチル-4-ビペリジル）セバケート、テトラ（2,2,6,6-テトラメチル-4-ビペリジル）-1,2,3,4-ブタンテトラカルボキシレート、2-〔（2,2,6,6-テトラメチル-4-ビペリジル）イミノ〕2-ブチル〔（2,2,6,6-テトラメチル-4-ビペリジル）イミノ〕、2-（3,5-ジ-*tert*-ブチル-4-ヒドロキシベンジル）-2-*n*-ブチルマロン酸ビス（1,2,2,6,6-ペンタメチル-4-ビペリジ

ル)等が挙げられる。

【0032】紫外線吸収剤としては、p-tert-ブチルフェニルサリシレート、2,4ジヒドロキシベンゾフェノン、2,2'-ジヒドロキシ-4-メトキシベンゾフェノン、エチル-2-シアノ-3,3'-ジフェニルアクリレート、2-エチルヘキシル-2-シアノ-3,3'-ジフェニルアクリレート、2(2'-ヒドロキシ-3'-tert-ブチル-5'-メチルフェニル)-5-クロルベンゾトリアゾール、2(2'-ヒドロキシ-3',5'-ジ-tert-ブチルフェニル)ベンゾトリアゾール、2(2'-ヒドロキシ-5'-メチルフェニル)ベンゾトリアゾール、2-ヒドロキシ-4-メトキシベンゾフェノン、2-ヒドロキシ-5-クロルベンゾフェノン、2-ヒドロキシ-4-オクトキシベンゾフェノン、2(2'-ヒドロキシ-4-オクトキシフェニル)ベンゾトリアゾール、フェニルサリシレート、2,2',4,4'-テトラヒドロキシベンゾフェノン等が挙げられる。

【0033】熱安定剤としての金属塩としては有機酸の金属塩、金属の酸化物、水酸化物、ゼオライト類、ハイドロタルサイト類等が挙げられる。

【0034】有機酸の金属塩の構成有機酸としては、プロピオン酸、カプリン酸、2エチルヘキシル酸、ネオオクタン酸、デカン酸、ミリスチン酸、オレイン酸、ステアリン酸、リノレイン酸、12-ヒドロキシステアリン酸、アジピン酸、セバチン酸、マレイン酸、安息香酸、トルイル酸、p-tert-ブチル安息香酸、サリチル酸、フタル酸、チオグリコール酸、メルカプトブ*

*ロピオン酸、チオジプロピオン酸等が、またフェノール、p-tert-ブチルフェノール、ノニルフェノール等のフェノール類が挙げられる。構成する金属としては、リチウム、ナトリウム、マグネシウム、カリウム、カルシウム、アルミニウム等が挙げられる。

【0035】本発明のポリ塩化ビニル樹脂系組成物で使用する充填剤としては、例えば軽質炭酸カルシウム、重質炭酸カルシウム、クレー、タルク、シリカ、けい素土、珪石粉、雲母粉、アルミナ硫酸アルミニウム、硫酸バリウム、ガラス繊維、カーボン繊維、グラファイト、木粉等が挙げられる。

【0036】本発明におけるポリ塩化ビニル樹脂系組成物は上記以外に一般的配合剤、すなわち帯電防止剤、発泡剤、顔料、蛍光剤、難燃剤、離型剤、抗菌剤等を使用することができる。

【0037】

【実施例】以下、実施例及び比較例によって本発明を具体的に説明するが、本発明はこれらによって限定されるものではない。

【0038】(過塩素酸処理ハイドロタルサイトの製造)ハイドロタルサイト類として協和化学工業(株)製のアルカマイザー-1を用いて、常法に従って過塩素酸処理し、アルカマイザー-1中の炭酸アニオンの所定の数量(20%、50%、60%、90%)を過塩素酸アニオンに置き替えた(表1)。

【0039】

【表1】

過塩素酸処理ハイドロタルサイト類 $\text{H}_2\text{Al}_2(\text{OH})_{12}(\text{CO}_3)_x(\text{ClO}_4)_{1-x} \cdot 3\text{H}_2\text{O}$

	X	Y
過塩素酸処理ハイドロタルサイト1	0.8	0.4
過塩素酸処理ハイドロタルサイト2	0.5	1.0
過塩素酸処理ハイドロタルサイト3	0.4	1.2
過塩素酸処理ハイドロタルサイト4	0.1	1.8

【0040】(実施例1)下記配合物を180°Cに調製した6インチオープンロールにより3分間連続、シートを作成した。このシートから適当な大きさの試験片を裁断し、190°Cに設定したギヤ式老化試験機に入れ、熱安定性試験を行った。ギヤ式老化試験機に入れたシートは所定時間ごとに採取し、それらの標準白色板に※40

※対するΔE値を色彩分析装置(COLOR ANALYZER TC-1800MK-11:東京電色株式会社製)により測定し、これを色調変化の指標とした。ΔEの値が小さいほど色調が良好であることを示している。

【0041】

(試験配合)

ポリ塩化ビニル樹脂(P=1050)	100
重質炭酸カルシウム	3
Ca-St	0.5
リクスターSL-02(理研ビタミン製)	0.5
ジフェニルトリデシルホスファイト	0.5
DOP	5.0
安定化剤	(表2)

【表2】

【0042】

実施例

	添加剤	未加 熱	10 分	20 分	30 分	40 分
比較例 1	なし	22.3	35.9	49.6	55.8	71.7
比較例 2	過塩素酸処理ハイドロタルサイト 3 0.3	21.4	33.1	45.5	46.8	50.2
比較例 3	ペンタエリスリトール 0.3	25.5	38.3	52.1	63.4	75.6
比較例 4	ジトリメチロールホペン 0.3	20.0	30.4	51.2	61.4	87.4
比較例 5	過塩素酸処理ハイドロタルサイト 3 0.3 ペンタエリスリトール 0.3	21.1	29.6	40.1	45.5	49.8
比較例 6	過塩素酸処理ハイドロタルサイト 3 0.3 ジベンゾイルメタン 0.1	25.6	39.2	48.2	51.3	65.6
比較例 7	アルカマイザー 1 0.3 ジトリメチロールホペン 0.3	34.7	43.5	60.1	72.9	89.9
実施例 1	過塩素酸処理ハイドロタルサイト 3 0.3 ジトリメチロールホペン 0.1	19.9	27.8	29.2	27.6	33.1
実施例 2	過塩素酸処理ハイドロタルサイト 3 0.3 ジトリメチロールホペン 0.3	19.4	23.3	25.2	26.7	32.3
実施例 3	過塩素酸処理ハイドロタルサイト 4 0.3 ジトリメチロールホペン 0.3	18.9	22.5	23.7	25.5	26.4
実施例 4	過塩素酸処理ハイドロタルサイト 2 0.3 ジトリメチロールホペン 0.3	19.5	26.6	28.8	29.1	35.1
実施例 5	過塩素酸処理ハイドロタルサイト 3 0.3 トリメチロールホペン 0.3	19.3	22.3	27.9	33.2	38.6
実施例 6	過塩素酸処理ハイドロタルサイト 3 0.3 ジトリメチロールホペン (M.V=約90 0) 0.3	20.2	29.8	35.2	37.3	39.5

【0043】実施例から明らかなように亜鉛化合物、スズ化合物、鉛化合物などの重金属を使用しない場合（比較例1）には、着色性が著しく、これに過塩素酸処理ハイドロタルサイト（比較例2）またはポリオール類（比較例3、4）を使用してもその効果は殆どなく、不十分である。過塩素酸処理ハイドロタルサイトとペンタエリスリトールとの両者を併用（比較例5）してもその効果は全く不十分である。

【0044】またハイドロタルサイトとジベンゾイルメタンを併用しても殆ど着色改善効果は認められない（比較例7）。

【0045】これに対して本発明に係る前記化1で表される過塩素酸処理ハイドロタルサイトと前記化2で表されるトリメチロール化合物類とを併用して使用した場合（実施例1～6）には、熱履歴の着色性の改善効果が著しいものである。

【0046】

【発明の効果】本発明によるポリ塩化ビニル樹脂組成物は、熱着色性に優れたものであり、あらゆる用途に好適に使用できる。特に重金属による汚染を嫌う半導体製造設備等の配水管などに好適に使用できる。